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# Pulsed laser deposition of diamond-like carbon films under a magnetic field

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**Abstract.** Pulsed laser deposition of diamond-like carbon films under a magnetic field has been studied. The magnetic field with its direction parallel to the surfaces of substrate and target can significantly enlarge the volume of green plume, and hence improve the uniformity. It has been found that not only the uniformity of thickness but also the hardness of films grown by this method were greatly improved. These diamond-like carbon films were analysed by atomic force microscopy and micro-hardness measurements. The root-mean-squared surface roughness of the films ($\approx 70$ nm) was about 0.265 nm. The hardness of films made by this technique can reach up to 6513 kgf mm$^{-2}$.

In the past few years, the pulsed laser deposition (PLD) method has been applied successfully to obtain high-quality diamond-like carbon (DLC) or even diamond films [1–6]. The high energy of the particles emitted from the graphite target has been used to deposit hard carbon films at relatively low substrate temperatures. However, the growth of DLC films with a uniform thickness by the PLD method represents a big challenge. The radial expansion of the ejected particles produces a domed profile of thickness [2]. Some authors have reported their efforts to make uniform DLC films, which were obtained by combining laser ablation of graphite target with some other auxiliary techniques [3, 4]. For example, Krishnaswamy *et al* used a 2 cm diameter graphite ring electrode and a corresponding discharge circuit to make the plume extend from the ablated spot to the ring and beyond up to the substrate [3]. The DLC films were grown uniformly on 3 cm$^2$ areas with improved optical and mechanical properties. Davanloo *et al* designed a new substrate-holder system in which the substrate carrier was able to rotate four discs 3.2 cm in diameter [4]. In this way, the dependence of deposition rate upon angular displacement from the input axis of the laser beam was compensated and films of good uniformity over an area of 8 cm$^2$ could be grown. In this paper, we report a new technique in which a magnetic field is incorporated between the graphite target and the substrate. As we know, the magnetic field is mainly effective for ionic species and these ionic particles are responsible for deposition of harder DLC films. So we attempted to use the magnetic field to deflect the beam of ionic particles in the pulsed laser deposition of DLC films. We found no apparent deflection of the ionic particles but enlargement of the plume volume. Although the reason for the expansion of the plume is not clear now, we continued the experiments and got the preliminary results. Uniform depositions over a significantly large area are characteristic of this deposition method, and the amorphous hard DLC films deposited by this method show increased hardness as compared to films deposited by the conventional pulsed laser deposition method. The technique is quite general and can be applied to a variety of materials.

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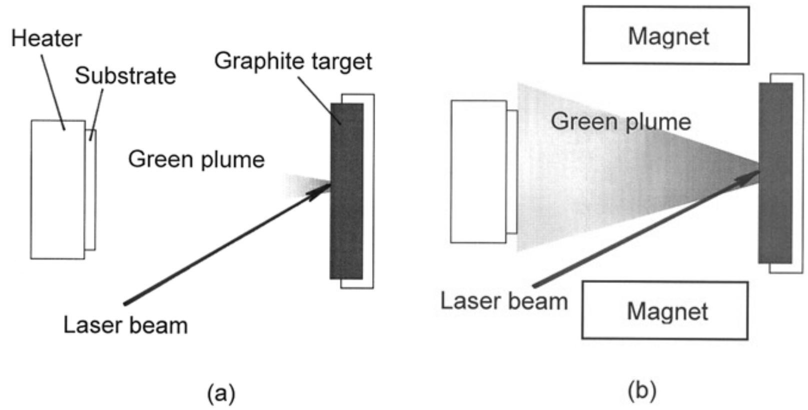

**Figure 1.** Schematic diagram illustrating (a) the conventional pulsed laser deposition method, and (b) with a magnetic field. The magnetic field is used to produce a large volume of green plume at the same laser energy density as in (a). The green plume is extended from the target to the substrate (≈6 cm).

The conventional setup for producing diamond-like carbon films by the pulsed laser deposition method is schematically shown in figure 1(a). The background pressure of the chamber was $5 \times 10^{-6}$ mbar. The distance between the substrate and the graphite target was typically 6 cm. An XeCl excimer laser with wavelength of 308 nm was used. The pulse energy was 270 mJ. The repetition rate was 10 Hz. The laser beam was focused by a lens onto the graphite target at a density of 4 J $\mathrm{cm}^{-2}$. Under these conditions the visible extent of the plasma plume (with a green colour) was small and only near the target surface region. The films deposited on Si(111) were hard and adherent. A schematic diagram of the pulsed laser deposition under magnetic field is shown in figure 1(b). Two permanent magnets of NdFeB with their N and S poles face to face were connected inside a U-shaped iron plate. The diameter and thickness of the magnet were 2.5 and 1 cm respectively. The magnetic fields in the middle part between the two magnets and on the surfaces of the magnets were 420 Gauss and 3960 Gauss respectively. The distance between the two magnets was 5 cm. A large green plume which extended from the ablated spot to the substrate was formed. This phenomenon was remarkable especially at a high laser energy density. It may be mentioned that in this preliminary study neither the value of magnetic field nor the distance between the two magnets was optimized. In order to monitor the effects of such a plasma on the properties of DLC films, two groups of samples were deposited under otherwise identical conditions except that one group of samples was deposited under magnetic field. The deposition time was twelve minutes for all samples. The films were deposited on Si(111) substrates at different temperatures. The magnetic field markedly altered the plume by extending it from the ablated spot to the substrate. With the help of the magnetic field, deposition was found to be more uniform and over a larger area as compared to the conventional method. Films produced by the conventional method usually showed a domed profile in thickness [2]. Figure 2 shows the spatial distribution of DLC films grown on a glass substrate with and without a magnetic field. The position at 2 cm is the centre of the deposition. The thickness of the conventional deposited DLC film was in the range from 40 to 130 nm, while that with a magnetic field changed between 30 and 80 nm as measured with a TENCOR P-10 surface profiler.

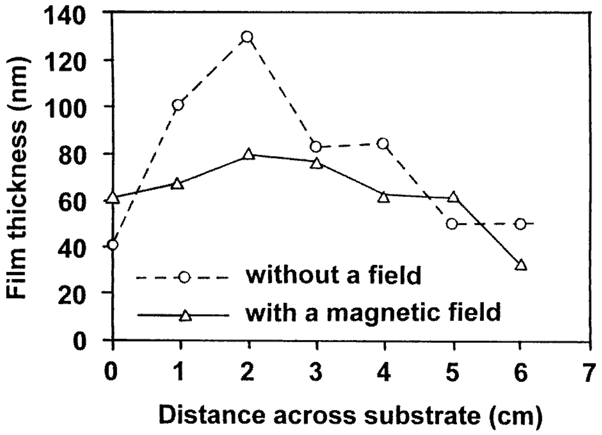

**Figure 2.** The spatial distribution of the thickness of diamond-like carbon films grown without magnetic field (upper curve), and with magnetic field (lower curve).

**Table 1.** Vickers micro-hardness of the diamond-like carbon films grown with and without the magnetic field. The micro-hardness of silicon is 1027 kgf mm$^{-2}$. The load and the dwell time are 50 gf and 10 s respectively.

| Deposition method | Substrate temperature (°C) | Film thickness (nm) | Hardness (kgf mm$^{-2}$) $H_c$ | Hardness (kgf mm$^{-2}$) $H_f$ |
|---|---|---|---|---|
| Without magnetic field | 25 | 67 | 1225 | 3030 |
| | 70 | 88 | 1283 | 2954 |
| | 105 | 70 | 1171 | 2454 |
| | 530 | 107 | 1346 | 2955 |
| With a magnetic field | 25 | 85 | 1449 | 4122 |
| | 70 | 75 | 1486 | 4794 |
| | 105 | 70 | 1693 | 6513 |

The surface morphology was studied by atomic force microscopy. The AFM tip was scanned on an area of 1000 nm × 1000 nm in air. The DLC films were grown on Si(111) substrates at different temperatures for twelve minutes. The thickness of the film was about 70 nm. The surfaces of the films were mostly mirror-like by optical microscope due to a small undulation of the surface. This small height fluctuation was imaged with atomic precision AFM. The root-mean-squared (rms) surface roughness is given for the surface area of interest. The nominal overall rms surface roughness of the film was about 0.265 nm which is close to that of silicon substrate. The magnetic field had almost no influence on the rms surface roughness. However, the rms surface roughness was sensitive to deposition temperature. Films deposited at a higher temperature usually had a larger surface roughness.

The micro-hardness measurements were carried out on a Shimadzu micro-hardness tester (Vickers). On each sample, indentations were made under a load of 50 gf and at least three impressions were made at such a load. Both diagonals were measured to eliminate the asymmetry of the diamond pyramid. Because the measured value of hardness was dependent on the thickness of the film and the hardness of the substrate, the corrected film hardness was deduced from the model reported by He *et al* [7]. The composite hardness (i.e. the hardness measured on the coated substrate) $H_c$ was calculated from the following value of micro-hardness

Distance along y-axis of the sample (cm)

(a)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 1171 | 1197 | 1254 | 1145 | 1486 | 1197 | 1449 |
| | 1283 | 1171 | 1346 | 1095 | 1789 | 1413 | 1564 |
| | 1449 | 1648 | 1072 | 927 | 1197 | 1693 | 1283 |
| | 1449 | 1072 | 1346 | 1283 | 1314 | 1693 | 1449 |
| 0 | 1413 | 1197 | 1072 | 1120 | 1605 | 1648 | 1254 |

0 1 2 3 4 5 6 7

(b)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 1486 | 1524 | 1449 | 1605 | 1374 | 1605 | 1605 |
| | 1120 | 1892 | 1524 | 1648 | 1413 | 1693 | 1648 |
| | 1283 | 1283 | 1789 | 1648 | 1524 | 1379 | 1564 |
| | 1283 | 1564 | 1605 | 1648 | 1605 | 1486 | 1648 |
| 0 | 1486 | 1524 | 1449 | 1648 | 1413 | 1693 | 1740 |

0 1 2 3 4 5 6 7

Distance along x-direction of the sample (cm)

**Figure 3.** Uniformity of micro-hardness of diamond-like carbon film deposited on Si(111) substrate without magnetic field (a), and with magnetic field (b). The size of each sample is $1 \times 7$ cm$^2$.

equation

$$H_c = H_s + [(m+1)t/mbD - t^{m+1}/mb^{m+1}D^{m+1}](H_f - H_s)$$

where $H_s$ and $H_f$ were the hardnesses of the substrate and the film respectively, $m = 1.2$, $b = 1$, and $D$ was the indentation depth. Results are summarized in table 1. These data are from measurements made at the centre of each film with a size of $1 \times 1$ cm$^2$. The hardness of films deposited at room temperature without a magnetic field was 3030 kgf mm$^{-2}$ and that at 105 °C was reduced to 2454 kgf mm$^{-2}$. This trend is similar to what has been reported earlier [3, 8]. The hardness of films deposited at 530 °C was increased to 2955 kgf mm$^{-2}$ although the resistivity was reduced considerably. The reduction in resistivity was easy to understand since the film became a graphite-like film [9]. The hardness of films deposited under magnetic fields was increased especially for films grown at high temperatures. Figure 3 shows the uniformity of micro-hardness of DLC films deposited on Si(111) substrates at room temperature for twelve minutes with and without magnetic field. The centre of the sample is the deposition centre. It can be seen that the micro-hardness of the DLC film deposited under magnetic field was very uniform in the centre of the sample and increased in a larger area of the sample. The study on symmetry of the results is under way now. The micro-hardness values may vary for the same sample due to the nonuniformity of film thickness as shown in figure 2 and particulates in the film. It is very common that the micro-hardness values may be different in the film. This is particularly true for measuring hard materials. These materials are usually brittle so the effect of particulates and defects is greatly magnified.

In summary, pulsed laser deposition under magnetic field is described. DLC films deposited by this technique were found to be superior to those produced by the conventional method with regard to their micro-hardness and uniformity. The substrate temperature remained close to ambient during deposition, thus paving the way for coatings on heat-sensitive substrates. The present method is very simple but may be used for a variety of materials.

## References

[1] Wagal S S, Juengerman E M and Collins C B 1988 *Appl. Phys. Lett.* **53** 187
[2] Collins C B, Davanloo F, Juengerman E M, Osborn W R and Jander D R 1989 *Appl. Phys. Lett.* **54** 216
[3] Krishnaswamy J, Rengan A, Narayan J, Vedam K and McHargue C J 1989 *Appl. Phys. Lett.* **54** 2455
[4] Davanloo F, Juengerman E M, Jander D R, Lee T J and Collins C B 1990 *J. Appl. Phys.* **67** 2081
[5] Polo M C, Cifre J, Sanchez G, Aguiar R, Varela M and Esteve J 1995 *Appl. Phys. Lett.* **67** 485
[6] Park Hwantae, Young-Kyu Hong, Kim Jim Seung and Park Chan 1996 *Appl. Phys. Lett.* **69** 779
[7] He J L, Li W Z and Li H D 1996 *Appl. Phys. Lett.* **69** 1402
[8] Hanabusa M, Suauki M and Nishigaki S 1981 *Appl. Phys. Lett.* **38** 385
[9] Sato T, Furuno S, Iguchi S and Hanabusa M 1988 *Appl. Phys.* A **45** 355